

AD-A236 978



2

Office of Naval Research

Final Report

for

1 August 1985 through 30 September 1989

for

Contract N00014-83-K-0638

Optical and Magnetic Spectroscopy at Interfaces of  
Strained Semiconductor Superlattices

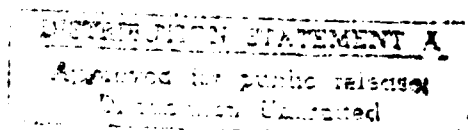
Arto V. Nurmikko

Brown University, Division of Engineering

Providence RI 02912



May 1991



91-01705



91 6 10 044

## I. Introduction

This document summarizes research activities in a rapidly developing area of compound semiconductor superlattices. The area concerns materials based on the II-VI and, to a lesser extent, on the IV-VI compound semiconductors. Advances in modern epitaxy have made it possible to generate versatile layered structures. The emphasis in the work described below was especially on ultrathin layer structures where individual constituent layers approach atomic dimensions (monolayer limit). The description below provides a summary of recent accomplishments under ongoing ONR support. The new opportunities which exist for the proposed research are very much based on the physical understanding in terms of specific microscopic phenomena which has been accumulated in the principal investigators laboratory in the past two years, in concert with collaborators elsewhere. Of general physical interest were electronic, magnetic, and vibrational excitations near the 2D limit, especially in circumstances where coupling of such elementary excitations was a factor. The research also has a applied connection to optical and magneto-optical devices such as modulators and magneto-optical switches and storage elements.

## II. Accomplishments Under the Grant (N00014-83-K0638):

### A Final Progress Review

In this section we describe the major accomplishments under the present grant in the period 1987-1989. The aim of the summary is to show that a range of new results have been obtained in relation to electronic and magnetic phenomena in compound semiconductor heterostructures which in most cases represent novel material configurations in their own right.

#### (a) Ultrathin Layer MnSe Superlattices (1987)

One of the intriguing recent developments in the preparation by advanced epitaxy of II-VI compound semiconductor superlattices involves the inclusion of magnetic constituents into selected spatial regions of the superlattice matrix. In particular, ultrathin layers of 'metastable'



zincblende form of MnSe has been incorporated to a ZnSe host [1] and there are initial efforts with Fe as the magnetic element in the same nonmagnetic base compound [2]. Such structures provide an unusual opportunity for the study of magnetic behavior in insulators at their interfaces and near the 2-dimensional limit. Conversely, magnetic phenomena which is sensitive to disorder effects on atomic scale can be useful in evaluating the quality of an interface on that spatial scale.

The new MnSe layered structures offer a great deal of structural versatility and may be ideally thought as magnetically 'tailorable'. For example, the spin wave spectrum in an ideal thin layer magnetic/nonmagnetic superlattice will significantly differ from that of a bulk magnetic semiconductor because of the altered boundary conditions and the 2D aspects of the problem. There is no experimental work in magnetic insulators in this area so far and substantial opportunities for fundamental research exist e.g. for examining collective magnetic excitations in novel and unusual circumstances. In longer term, tunable magnetic devices can also be considered.

Before magnetic semiconductor structures of ideal precision can be prepared, however, a major set of practical and fundamental questions must be answered concerning the interface aspects of a real superlattice. In case of an early prototype such as the MnSe/ZnSe system, the nature of the molecular beam epitaxial growth and the lattice mismatch strain both contribute to finite microscopic disorder at each heterointerface. Assuming a layer-by-layer growth mode, imperfections in the form of finite 2D islands (of MnSe or ZnSe) may occur at an interface for deviations from perfect monolayer coverage. These will depend critically on the details of growth conditions. Furthermore, in material systems which require a high substrate growth temperature, interdiffusion of constituent elements can take place, leading to a diluted magnetic semiconductor-like graded interface. Because the magnetic interactions are inherently of very short range in the semiconductors considered here (nearest neighbor dominated), phenomena such as ordering near the 2D-limit can be interrupted quite efficiently by disorder on the scale of the lattice constant (5-6 Å). To put this another way, study of the magnetic properties can provide uniquely microscopic diagnostic concerning the interface perfection in a artificially layered structure on a spatial scale which is difficult to reach by other analytical techniques such as

transmission electron microscopy or X-ray diffraction.

Examples of such interface sensitivity can be found from our recent ONR sponsored work with the MnSe/ZnSe superlattices. Optical investigations, based on photoluminescence, showed that from the standpoint of extended electron (Bloch-like) states, the structures were quite sound. This is illustrated in Figure 1 which shows the PL from a MnSe/ZnSe superlattice with 45 Å ZnSe layers (potential wells) separated by approximately 9 Å MnSe layers (3 monolayers of MnSe per superlattice period). The emission is well above that of the ZnSe bandgap (thus reflecting the existence of a superlattice potential) and has a reasonably narrow linewidth. Surprisingly, however, the PL emission is subject to a large Zeeman effect in an external magnetic field. The effect, which originates from the exchange interaction of the Bloch-like superlattice extended states with those of the Mn-ion d-electron localized spins, should be small if the Mn-ion system ordered in the normal antiferromagnetic sense. The size of the Zeeman effect thus suggests that anomalously large magnetizations can be induced in the ultrathin MnSe layers. Some of the Zeeman shifts are shown in Figure 2.

Direct magnetization measurements support these notions, as illustrated in Figure 3 where magnetization in a low external field (1 kG) is shown as a function of temperature for the MnSe/ZnSe superlattice structure in question, together with a sample of 10 monolayers of MnSe per SL period, and a MnSe thin epitaxial film (antiferromagnetically ordered). The temperature dependence for the 3 ML sample is nearly a paramagnetic one and its magnitude at low temperatures suggests that up to 20 % of the Mn-ion spins in the ultrathin layer superlattice are acting as if nearly free. With increasing MnSe layer thickness the magnetization measurements show an additional contribution superposed on signals such as in Fig. 3; these are at present attributed to a 'core' contribution from the center parts of the layers which have retained at least partially ordered antiferromagnetic character. The 'loose spin' population is, in this interpretation, a product of the immediate interface region. Clearly, the details of the remaining spin-spin interactions for this population depend decisively on the microscopic geometrical features at the interface; this is particularly the case with exchange paths involving an intervening anion (Se).

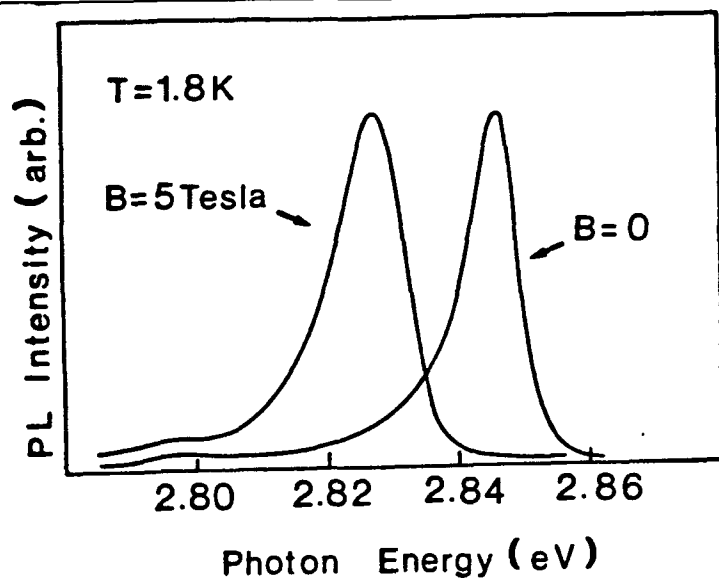


Figure 1: Exciton luminescence at the SL bandgap for the 10 ML sample at  $T=2\text{ K}$ , and circularly polarized emission in 5 Tesla field.

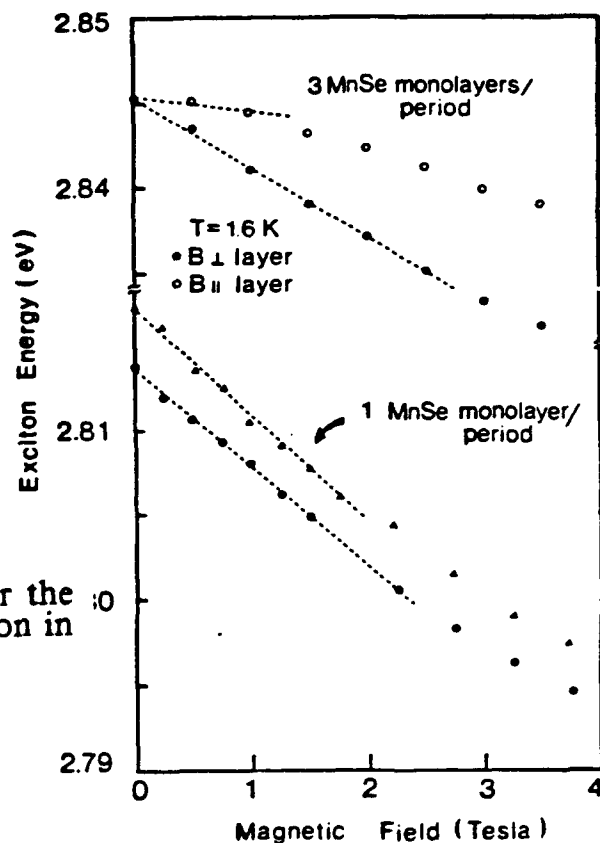


Figure 2: Zeeman shifts for 1 ML and 3 ML SLs at  $T=1.6\text{ K}$ . Triangles and dark circles refer to 1 ML structures with and without growth interruption. Field anisotropy is shown for the 3 ML case; here also growth interruption (not plotted) affected only a small change in the slope of the low field Zeeman shift (dashed lines to guide eye).

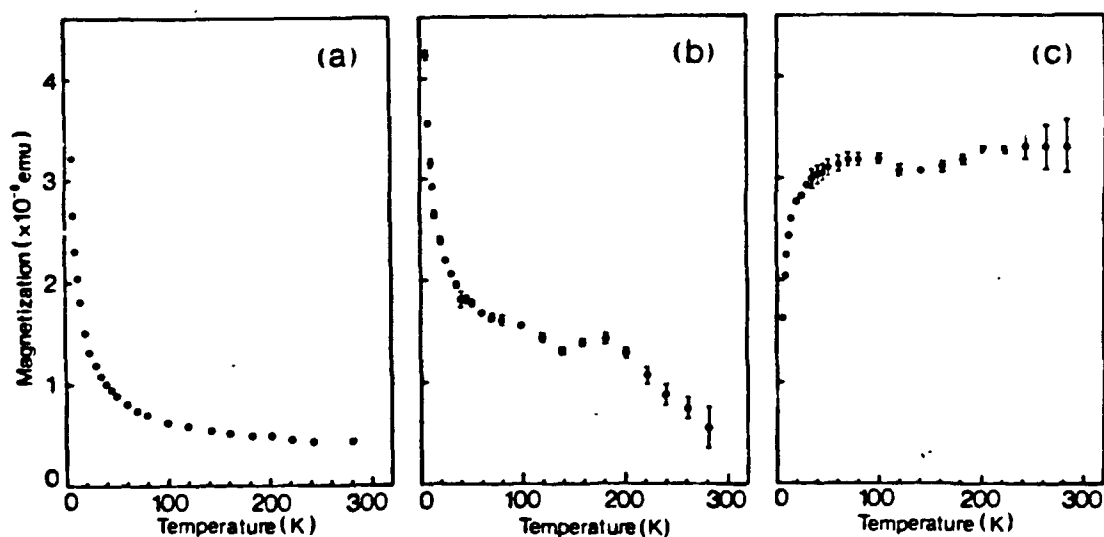


Figure 3: Magnetization as a function of temperature for (a) 3 ML SL, (b) 10 ML SL, and (c) MnSe film. Substrate and buffer layer contribution has been subtracted.

## References:

- [1] L.A. Kolodziejewski, R.L. Gunshor, N. Otsuka, B.P. Gu, Y.Hefetz, and A.V. Nurmikko, Appl. Phys. Lett. **48**, 1482 (1986)
- [2] B. Jonker, J. Krebs, S. Qadri, and G. Prinz, Appl. Phys. Lett. **50**, 848 (1987)

### (b) Isoelectronic Delta Doping of ZnTe Superlattices (1988 and ongoing)

In this work we have gained direct microscopic insight about localization of excitons in a II-VI superlattice of potential optoelectronic importance. Specifically, we have focused on isoelectronic doping of ZnSe/(Zn,Mn)Se quantum wells by Te, achieved in a nearly two-dimensional way by the deposition of approximately monolayer thick ZnTe 'sheets' into these structures. The presence of the added ZnTe layers dramatically alters the exciton recombination spectra; this is principally due to strong trapping effects, accompanied by local lattice distortion, at the 'delta-doped' Te isoelectronic centers.

Data is here summarized for one multiple quantum well structure (MQW) of ZnSe/Zn<sub>1-x</sub>Mn<sub>x</sub>Se ( $x=0.21$ ), grown by molecular beam epitaxy at Purdue University, with a molecular monolayer on ZnTe incorporated in the middle of each ZnSe quantum well [1]. Comparison between photoluminescence (PL) spectra of an undoped MQW ( $L_w=67$  Å) and one including the 'delta-doping' ( $L_w=44$  Å) is shown in Figures 4a and 4b, respectively. Both structures were highly quantum efficient ( $T=2$  K); the PL amplitudes are normalized in the figure. The emission in Fig. 4a is dominated by quasi-2D  $n=1$  exciton. Figure 4c shows the PL excitation spectrum for the Te-doped structure displaying the principal  $n=1$  exciton absorption features (light and heavy hole exciton, respectively), characteristic also of undoped structures [2]. The addition of an ultrathin 'sheet' of ZnTe has only a minor effect on the absorbing exciton.

The large Stokes shifts (100-300 meV) and the prevalence of broad features ( $> 100$  meV) in the delta-doped structures have earlier been observed in the dilute bulk alloy ZnSe<sub>1-x</sub>Te<sub>x</sub> for

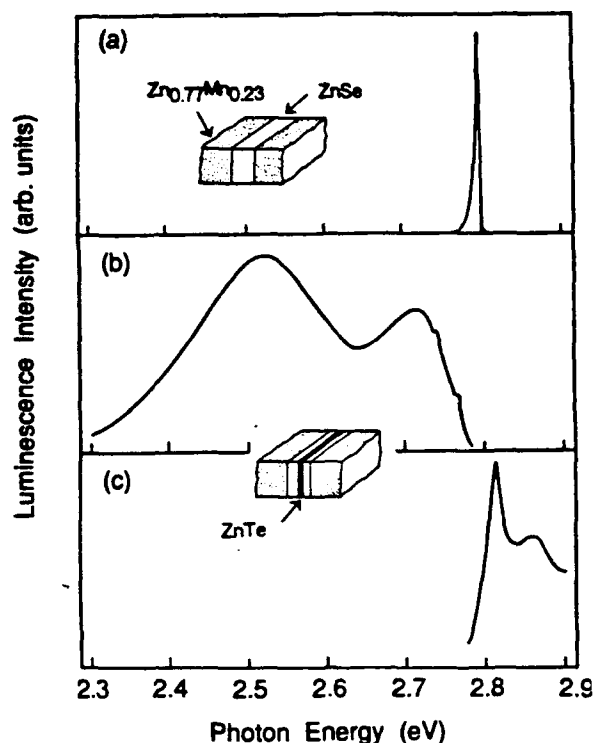


Figure 4: Luminescence from a reference ZnSe/(Zn,Mn)Se quantum well sample (a) and a Te 'delta-doped' structure (b). The excitation spectrum of the latter is shown in (c) near  $n=1$  exciton transition. ( $T=2\text{K}$ ).

Figure 5: (a) Zeeman effect at  $T=2\text{K}$  in the excitation spectrum of the doped structure, showing the  $n=1$  exciton splitting in 3 Tesla field (dotted line); (b) portion of the luminescence spectrum with and without magnetic field (solid and dotted lines, respectively)

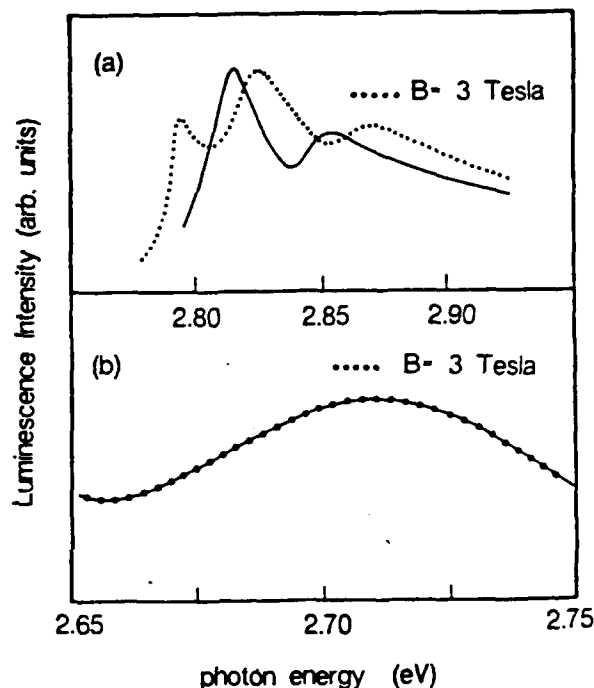
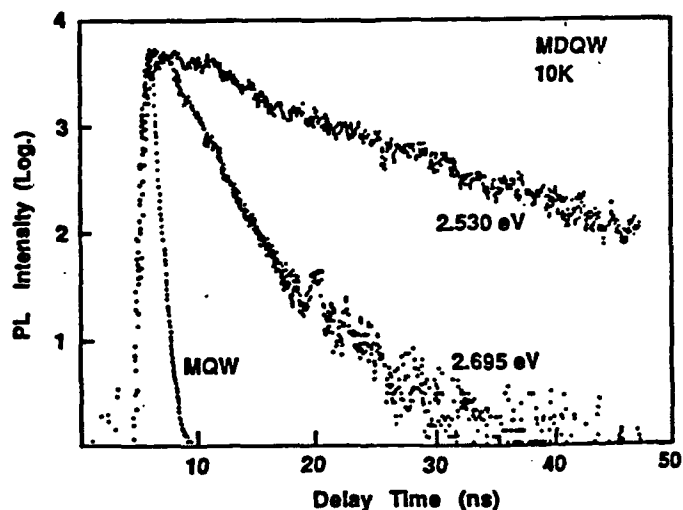


Figure 6: Transient luminescence from an undoped ('MQW') and iso-electronically doped ('MDQW') ZnSe quantum well. The exciton decay rate for the latter is shown at two photon energies corresponding to the binding to different Te complexes at the center of the quantum well.



$x < 0.05$  [3],[4]. Our interpretation [4] evokes self-trapping of excitons at small Te clusters, with single Te-sites and double Te-sites (Te atoms on nearest neighbor anion sites), associated with the higher and lower energy peaks at 2.72 eV and 2.53 eV in Fig. 1b. This is consistent with approximately one monolayer worth of interdiffusion at the ultrathin ZnTe sheets so as to produce a thin ( $\sim 6$  Å) region of  $\text{ZnSe}_{1-x}\text{Te}_x$  at the center of each ZnSe quantum well.

The presence of the diluted magnetic semiconductor,  $\text{Zn}_{1-x}\text{Mn}_x\text{Se}$ , in the superlattice is useful due to its large effective g-factor. This means that exciton Zeeman splittings are directly related to wavefunction penetration into the barrier layers. Figure 5 compares the field induced effects in both excitation and PL spectra in a 3 Tesla field at  $T = 2\text{K}$  parallel to the superlattice growth axis ( $z$ ) for the delta-doped sample. Only a small portion of the PL spectrum is shown near the higher energy peak (note expanded horizontal scale); however, similar conclusions apply to the entire spectrum. While the excitation spectrum (absorbing exciton) shows a large Zeeman splitting of approximately 30 meV of the  $n=1$  exciton ground state, the emission spectrum shows a much reduced effect corresponding to at most a 1 meV spectral shift. Our analysis of this experimental data, based on the previously determined approximate bandoffsets and known exchange coefficients for  $\text{Zn}_{1-x}\text{Mn}_x\text{Se}$ , is that the effective Bohr diameter of hole wavefunction associated with the recombining exciton (in  $z$ -direction) has collapsed to the size of approximately a lattice constant in the self-trapping process at the Te sites in the middle of the quantum well. At the same time, additional spectroscopy including polarization studies [5] shows that the electron component of the exciton undergoes very little change. One direct consequence of this is a large change (reduction) in the recombining exciton oscillator strength upon self-trapping. Reflecting this, the radiative lifetimes shown in Figure 6 vary in the range of 10-50 nsec (depending on quantum well width and other structural parameters) while a typical value for the latter is about 200 psec at low lattice temperatures where radiative processes dominate. The decay of the exciton in an unmodulated quantum well sample ('MQW') is short and not fully time resolved here. The exciton lifetime in the Te delta-doped quantum well ('MDQW') sample is shown at two spectral corresponding to the peaks in spectrum of Fig. 3b. The more rapid decay of the higher energy peak reflects energy transfer between the two types of trap sites along the Te-doped layer plane. The decay of the lower energy feature, on the



other hand, is dominated by radiative recombination. Additional details of these kinetic measurement lifetime will be reported elsewhere [6].

## References:

- [1] L.A. Kolodziejski, R.L. Gunshor, Q. Fu, D. Lee, A.V. Nurmikko, and N. Otsuka, Appl. Phys. Lett., **52**, 1080 (1988)
- [2] Y. Hefetz, J. Nakahara, A.V. Nurmikko, L.A. Kolodziejski, R.L. Gunshor, and S. Datta, Appl. Phys. Lett. **47**, 989 (1985)
- [3] A. Reznitsky, S. Permogorov, S. Verbin, A. Naumov, Yu. Korostelin, V. Novozhilov, S. Prokov'ev, Solid State Comm. **52**, 13 (1984)
- [4] D. Lee, A. Mysyrowicz, A.V. Nurmikko, and B.F. Fitzpatrick, Phys. Rev. Lett. **58**, 1475 (1987)
- [5] Q. Fu, D. Lee, A.V. Nurmikko, L.A. Kolodziejski, and R.L. Gunshor, submitted to Phys. Rev. B
- [6] D. Lee, Q. Fu, A.V. Nurmikko, L.A. Kolodziejski, and R.L. Gunshor, Superlattices and Microstructures (in press)

## (c) Determination of Bandoffsets in the CdTe/(Cd,Mn)Te Quantum Well (1987-88)

In this work we have performed magneto-optical experiments to provide first precise measurements for bandoffsets in a wide gap II-VI heterostructure. The barrier material with 'giant' g-factors gives a significant experimental advantage in that the quantum well barrier heights can be substantially altered in a given sample by external fields to provide a wide basis of data for analysis without sample-to-sample uncertainties. However, in order to bring theory and experiment into agreement, it is critical to include properly the excitonic effects which, under conditions of a small valence bandoffset, add to the net potential well for the hole due to the electron Coulomb interaction. The final bandoffset by our determination is believed to be accurate to better than 10 meV; this makes the optical methods attractive when compared against e.g. photoemission methods.

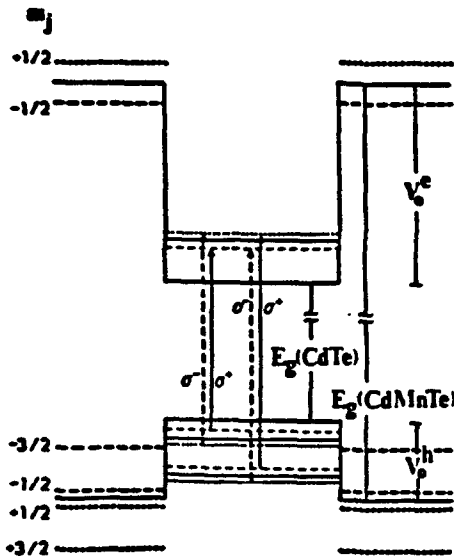


Figure 7: Schematic of influence of magnetic field on a CdTe/CdMnTe quantum well in electron-hole representation

Figure 8: Excitation spectra for the  $n=1$  HH and LH exciton in (a) zero field; (b) 4 Tesla field parallel to QW axis; and (c) 4 Tesla field perpendicular to QW axis.  $T=2K$ .

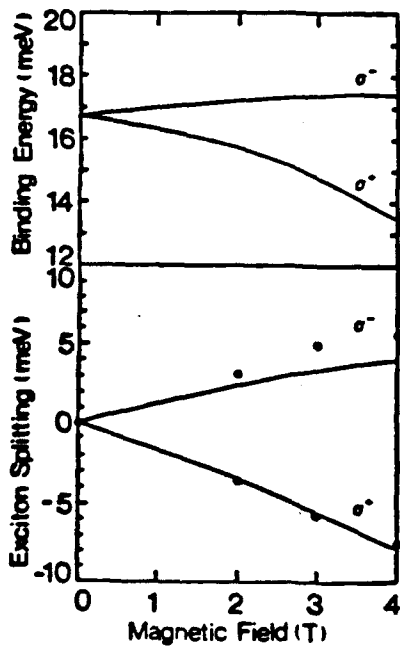
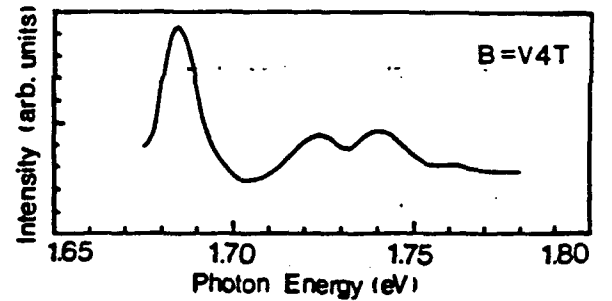
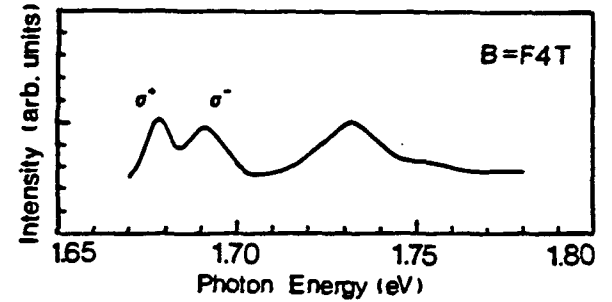
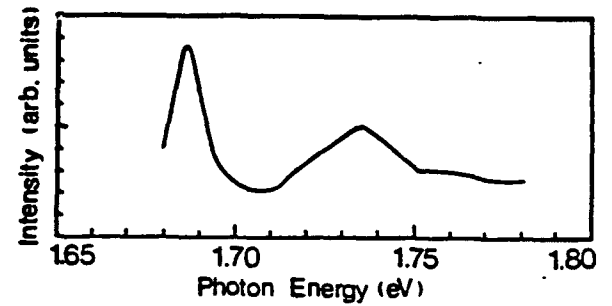


Figure 9: (lower panel) Comparison of experiment (dots) and theory (with 25 meV offset) for Zeeman splitting of the  $n=1$  HH exciton; upper panel: calculated field induced changes in exciton binding energy.

**Figure 7** depicts the influence of a magnetic field on a CdTe/(Cd,Mn)Te quantum well with circularly polarized optical transitions in Faraday geometry indicated. **Figure 8** shows portion of the excitation spectrum for a MQW sample with CdTe well thickness of 50 Å at  $T=2\text{K}$  in zero field (a), and in a field of 4 Tesla near the  $n=1$  exciton resonance (b) and (c). The two principal features in Fig. (1a) are the HH and LH (light hole) excitons, respectively (with masses referred to the  $z$ -direction of the superlattice axis). In addition, we also obtained from the excitation spectra at higher photon energies the transitions for the  $n=2$  HH exciton at 1.925 eV and that for the (Cd,Mn)Te alloy barrier at 1.990 eV. **Figure (8b)** shows the splitting of the  $n=1$  HH exciton by 13 meV for the field in the direction of the superlattice axis ( $B_z$ ). This is also to the Faraday configuration and well defined circular polarization selection rules are obeyed, as indicated in the figure (which is actually a superposition of two excitation spectra obtained for opposite circular polarizations).

A summary of the  $n=1$  HH exciton splitting is shown in **Fig. 9** as a function of the applied field (bottom panel). The figure also includes results of our calculations (solid lines) with specific bandoffset values and exciton binding energies described below. We have used the experimental data as input to a calculation in the envelope function approach where the problem of an exciton in a DMS quantum well is solved by variational means [1] which differ in character from those applied e.g. for type I GaAs quantum wells. In wide gap II-VI semiconductors, exciton binding energies are sizable, approximately 10 meV for bulk CdTe. In the context of a quantum well this means that the one particle envelope functions are more tightly bound than simply expected from the 'structural' quantum well potentials  $V_c^s(B)$  and  $V_v^s(B)$  in the conduction and valence bands, respectively. In our approach it is natural to consider effective confinement for the electron and the hole by 'effective' potentials  $V'_c$  and  $V'_v$  which include the effects of Coulomb interaction and are used as additional variational parameters. The proper inclusion of the Coulomb interaction is particularly important in the case where one of the bandoffsets is small since the more weakly confined particle is particularly susceptible for the Coulomb field in the  $z$ -direction. The exchange splitting of the conduction and valence band states were included into the starting Hamiltonian in a usual way for DMS materials. Details of our calculations will be found in [2].

The good agreement between experiment and theory serves as an additional demonstration of the consistency of our calculations. For the MQW structure in question, the conduction band offset is approximately 360 meV, reflecting a band offset ratio of about 14 to 1. We may then extrapolate (neglecting mixing of the  $|m_j| = 3/2$  and  $|m_j| = 1/2$  states) that in the 'strain-free' limit of the (001) CdTe/(Cd,Mn)Te heterojunction the net effective bandoffset  $V_o^h$  for the HH valence band in the square well model considered here is zero on the scale of 10 meV. Similar conclusion is also reached for the LH band which is probably slightly type II in this limit.

#### References:

- [1] S.-K. Chang, A.V. Nurmikko, J.-W. Wu, L.A. Kolodziejski, R.L. Gunshor, Phys. Rev. B37, 1191 (1988)
- [2] J.-W. Wu and A.V. Nurmikko, Phys. Rev. B38, 1504 (1988)

#### (d) PbTe Based Heterostructures

##### - Optical Properties of (Pb,Eu)Te Thin Films and Superlattices (1987-88)

The developments in molecular beam epitaxial growth of (Pb,Eu)Te have recently amply demonstrated the usefulness of this material in infrared optoelectronic applications, especially as low threshold injection lasers in quantum well heterostructures. In the devices to date, the Eu-concentrations have been relatively low ( $x < 0.10$ ). Initial characterization of e.g. PbTe/(Pb,Eu)Te quantum wells in terms of basic electronic properties has in this case been relatively successful as the relevant electronic states of (Pb,Eu)Te can be assumed to be PbTe-like (p-like at L-point). However, the bandgap of (Pb,Eu)Te is seen to vary anomalously beyond  $x > 0.10$  as reported recently [1]. Here we report of this work to higher Eu concentrations (up to  $x = 1$ ) and discuss some early results from related superlattice structures.

### (a) (Pb,Eu)Te single crystal films

The samples used in these studies were MBE grown single crystal films of (Pb,Eu)Te on (111) oriented BaF<sub>2</sub> substrates. However, nonstoichiometric growth in excess Te vapor usually leads to p-type material with hole density on the order of  $1\text{-}2 \times 10^{17} \text{ cm}^{-3}$ .

A summary of the optical gap data is given in Figure 10 which displays the effective bandgap in (Pb,Eu)Te at  $T = 10\text{K}$  (onset of strong absorption with a well defined edge) as a function of the Eu-composition. Beyond a composition range of approximately  $x = 0.30$ , an increasing Stokes shift is seen to occur between the absorption edge and the associated luminescence emission. The dashed lines are to guide the eye and correspond to the following approximate slopes: in the low energy region ( $x < 0.05$ )  $dE_g = 5.8 \text{ eV}$ , and in the high energy region  $dE_g = 2.1 \text{ eV}$ . Measurements of Zeeman shifts in photoluminescence have been recently made by us to show that relatively small effective interband g-factors resulting from p-f exchange are typical in (Pb,Eu)Te at moderate concentrations ( $x < 0.20$ ); these are approximately one order of magnitude smaller than in II-VI and IV-VI DMS materials with Mn as the magnetic ion (the f-f exchange is also substantially weaker).

The absorption edge in EuTe (which shows several distinct features) is generally considered to onset with the 4f to 5d ( $t_{2g}$ ) Eu-ion transition (the corresponding luminescence Stokes shifts include a configurational relaxation which might contain magnetic polaron effects). Therefore, as Eu-in concentration is increased in (Pb,Eu)Te, one expects the eventual appearance of the 4f state ( $S = 7/2$ ) within the p-p bandgap, the latter defining the absorption edge in PbTe. We assign the observation of the incipient Stokes shift at approximately  $x = 0.30$  to such 'crossover' behavior.

### Reference:

- [1] A. Krost, et al. J. Phys. C, 18, 2119 (1985)

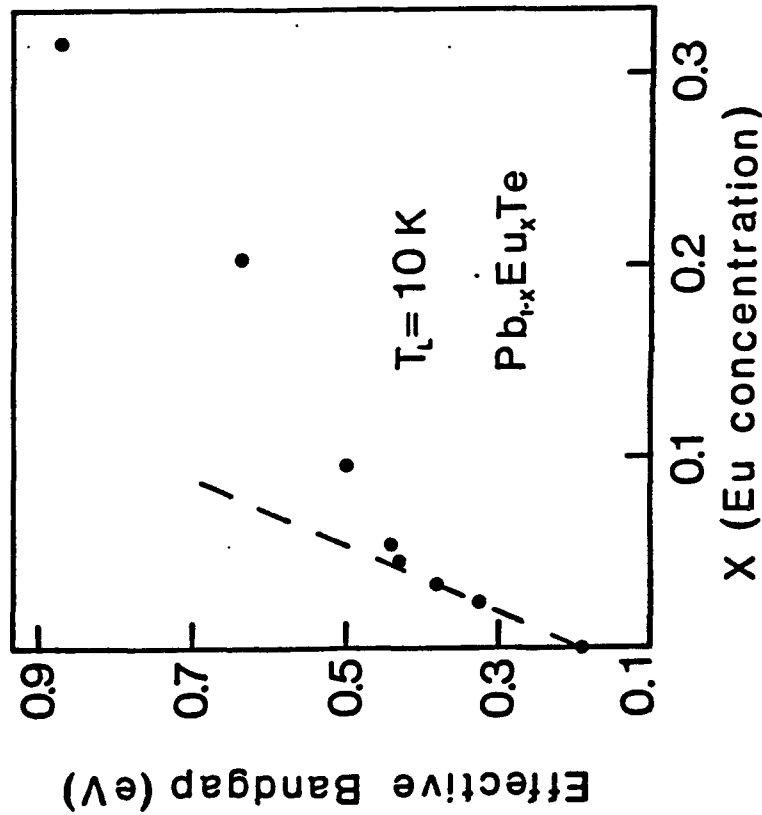


Figure 10: Optical gap of  $(\text{Pb},\text{Eu})\text{Te}$  as a function of Eu concentration at  $T=10\text{ K}$  as obtained from luminescence and absorption measurements. The dashed line is an empirical extrapolation in the low concentration limit.

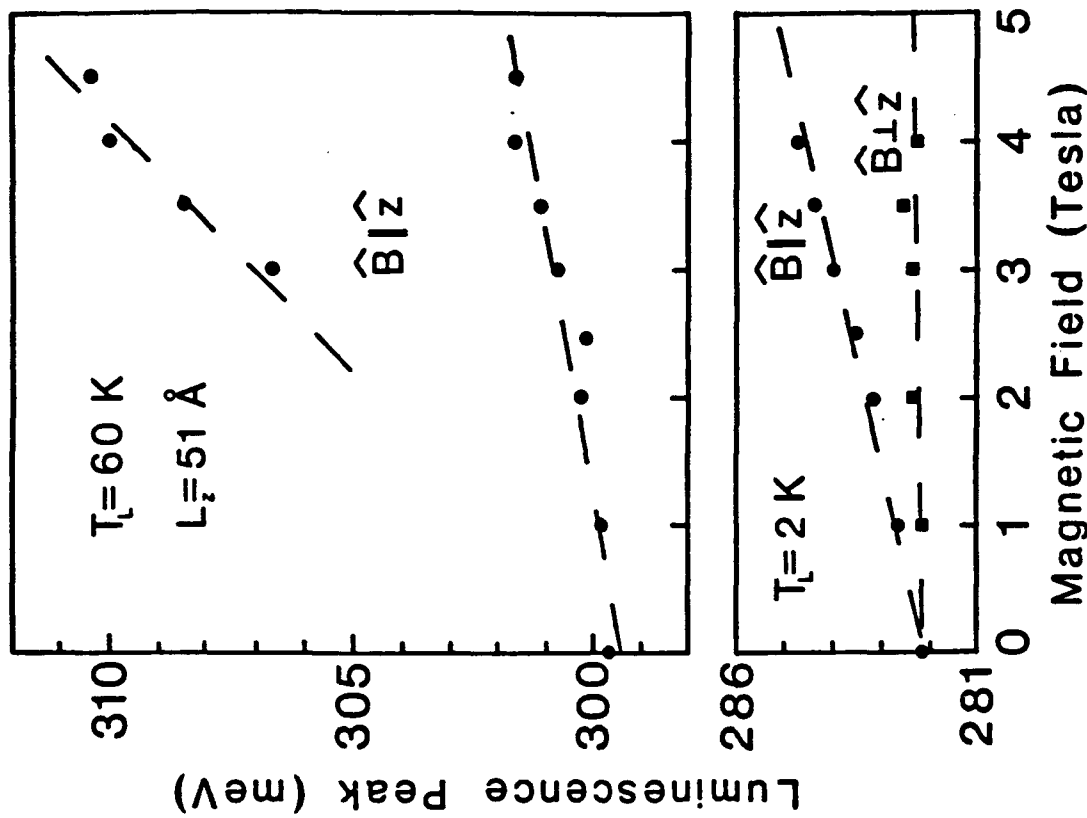


Figure 11: Influence of an external magnetic field on the position of the photoluminescence energy of a  $51\text{ Å}$   $\text{PbTe}$  quantum well. Lower trace: Dependence of field orientation versus superlattice axis at  $T = 2\text{ K}$ . Upper trace: Lowest resonance and the appearance of the next spin/Landau level transition at  $T = 60\text{ K}$ .

## (b) (Pb,Eu)Te Superlattices

Basic electronic properties of PbTe/(Pb,Eu)Te superlattices and multiple quantum wells have been studied in connection with laser development [1,2] and in other spectroscopic studies of these structures [3,4] at low concentrations of the Eu-ion in the barrier layers. The structures are of high quality as evidenced by their excellent luminescent efficiencies and spectral signatures typical of a quasi-2D electron-hole plasma. This is also clear from well behaved magnetic field effects such as in Figure 11 which shows the cyclotron anisotropy of the lowest spin-Landau level interband transition at 2K for a structure of PbTe well width  $L=51$  Å and  $x=0.04$  (lower panel) [8]. The next interband transition is also visible at an elevated temperature (upper panel).

We have recently also studied some optical properties of PbTe/EuTe superlattices grown either on PbTe or BaF<sub>2</sub> substrates. Unlike the structures with lower Eu-concentration in the barrier layers, where the addition of a Se constituent (up to 5%) facilitates a nearly strain free superlattice, the PbTe/EuTe structures are highly strained. This is clear, among other indicators, from the appearance of a relative robust signature in Raman scattering from optical phonons [5] which is symmetry forbidden in bulk PbTe and EuTe (in the latter spin dependent interactions give rise to a finite but weak Raman process). We have investigated the signature of the superlattice bandgap through photoluminescence and reflectance techniques; the emission is characterized by a broad transition with a peak at approximately 330 meV (in contrast, spontaneous emission from PbTe/(Pb,Eu)Te structures at low Eu-concentrations had linewidths less than 5 meV at low temperatures). To verify that the luminescence is an indicator of the superlattice bandgap, photomodulated reflectance spectrum was also measured (lower panel in the figure). Its lineshape is qualitatively in agreement with expectations for a simple interband transition; however, significant damping is also implied by the broad linewidth. A Kronig-Penney calculation is in reasonable with the observed superlattice bandgap which has nearly doubled from the value of bulk PbTe. Origin of the spectral broadening may involve mixing of the superlattice states with the Eu-ion f-electron states in the barrier layers; early magnetic field experiments have not yet given sufficiently clear indicators about the role of such complications. Nonetheless, the PbTe/EuTe superlattices presents intriguing prospects for further research as a

rare combination of a narrow bandgap and a magnetic semiconductor.

## References:

- [1] D.L. Partin, Appl. Phys. Lett. 45, 487 (1984)
- [2] D.L. Partin and C.M. Thrush, Appl. Phys. Lett. 45, 193 (1984)
- [3] W. Goltsos, J. Nakahara, A.V. Nurmikko, and D.L. Partin, Appl. Phys. Lett. 46, 1173 (1985)
- [4] W. Goltsos, J. Nakahara, A.V. Nurmikko, and D.L. Partin, Surface Sci. 174, 288 (1986)
- [5] S.-K. Chang, H. Nakata, and A.V. Nurmikko, unpublished

## - Free Carrier Radiative Recombination in 2D: PbTe Quantum Wells (1988)

There have been a number of studies aimed at isolating radiative recombination in semiconductor quantum wells, a process which in many instances is strongly influenced by excitonic effects such as in III-V (e.g. GaAs [1]) or wide-gap II-VI (e.g. ZnSe [2]) semiconductor heterostructures. In narrow-gap semiconductors, such as PbTe, excitonic effects are negligible; therefore quantum wells from these materials offer a clear opportunity to study quasi-2D free carrier radiative recombination over a wide temperature and density. We show here that radiative recombination dominates in high quality MBE-grown PbTe/(Pb,Eu)Te MQW's. At the same time PbTe/(Pb,Eu)Te based heterostructures show excellent prospects as low threshold diode injection lasers at mid-infrared wavelengths [4].

Direct time-resolved experiments on a subnanosecond timescale were performed by an up-conversion scheme shown in Figure 1, where the source of excitation was a modelocked cw Nd:YAG laser. The infrared PL emitted by the samples was combined with the main portion of the 1.06  $\mu\text{m}$  beam at a crystal of AgGaS<sub>2</sub>, appropriately oriented for phasematched operation for sum-frequency generation, and a delay stage was used to provide a nonlinear optical gate for direct time-resolved luminescence (PL) of the infrared signals.



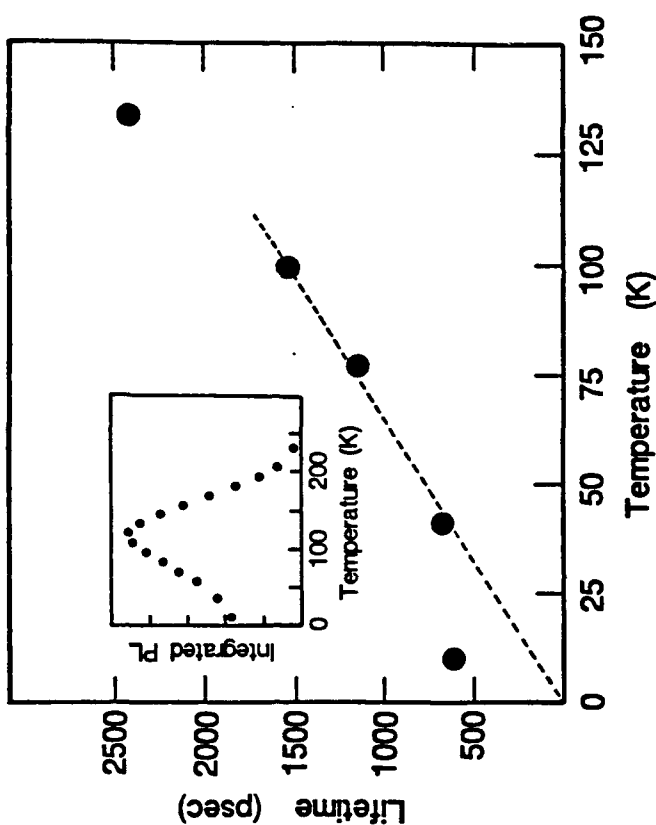


Figure 13: Lifetime of photoexcited quasi-2D electron hole pairs as a function of temperature (MQW sample with  $L_w=92$  Å); the dashed line shows prediction for linear temperature dependence in the nondegenerate density regime.

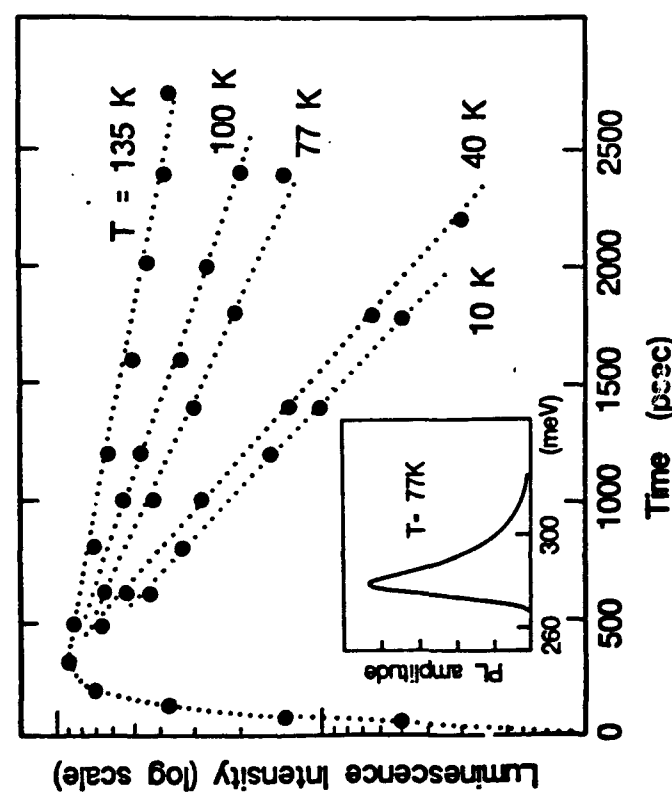


Figure 12: Transient luminescence (log scale) from a PbTe/(Pb,Eu)Te MQW sample of well width  $L_w= 92$  Å at different temperatures. The amplitudes are normalized. The inset shows the steady state PL spectrum in the infrared.

Figure 12 shows the time-resolved, upconverted PL from a PbTe/(Pb,Eu)Te MQW sample with  $L_w = 92$  Å, corresponding to the  $n=1$  conduction to valence band confined particle transition, at different temperatures on a semilogarithmic scale (normalized peak amplitudes). The inset shows the steady state PL spectrum at 77K for reference. Identifying the time constants with carrier lifetimes, a summary of their temperature dependence is plotted for several temperatures in Figure 13. The dashed line is a guide to the eye to show that the decay time increases nearly linearly over an appreciable temperature range. This dependence is consistent with radiative recombination in a nondegenerate or weakly degenerate 2D free carrier gas in our MQW structures. In particular, the carrier decay rates directly reflect the presence of a significant background hole density in the PbTe wells, generated as a consequence of (unintentional) modulation doping due to systematic stoichiometric deviations in the (Pb,Eu)Te barrier layers [5].

Under conditions of a 2D nondegenerate electron hole gas, it is straightforward to show that the expected lifetime due to spontaneous emission is proportional to  $kT/p_{\infty}$ , assuming a hole background with  $p_{\infty}$  the equilibrium density ( $\text{cm}^{-2}$ ). We have found that very good quantitative agreement can be reached with experiment assuming complete 'modulation doping' for maximum transfer of  $p_0 \approx 2 \times 10^{17} \text{ cm}^{-3}$  holes from (Pb,Eu)Te barrier layers to PbTe wells. At low temperatures, the lifetime in our MQW samples is nearly temperature independent. This has a contribution from the onset of strong degeneracy but as well as from incomplete modulation doping. At high temperatures, some of the extra lengthening in carrier lifetime reflects finite thermal excitation of holes in the PbTe wells from the  $n=1$  state either to  $n=2$  or the continuum states. The radiative recombination rates can also be strongly influenced in external magnetic fields (anisotropically) due to Landau quantization of the quasi-2D density of states.

#### References:

- [1] J. Feldmann, G. Peter, E. Gobel, P. Dawson, K. Moore, C. Foxon, and R.J. Elliott, Phys. Rev. Lett. **59**, 2337 (1987)
- [2] Y. Hefetz, W.C. Goltsos, D. Lee, A.V. Nurmikko, L.A. Kolodziejski, and R.L. Gunshor, Superlattices and Microstructures **2**, 455 (1986)

- [3] T. Matsusue and H. Sakaki, Appl. Phys. Lett. **50**, 1429 (1987)
- [4] D.L. Partin, Appl. Phys. Lett. **45**, 487 (1984)
- [5] J. Heremans, D.L. Partin, P.D. Dresselhaus, M. Shayegan, and H.D. Drew, Appl. Phys. Lett. **48**, 928 (1986)

**Publications from Current ONR Grant Research:**

"Anomalous Magneto-Optical and Magnetic Behavior in a Two-Dimensional Magnetic Semiconductor Superlattice MnSe/ZnSe", D. Lee, S.-K. Chang, H. Nakata, A.V. Nurmikko, L.A. Kolodziejski, and R.L. Gunshor, Proc. Mat. Soc. Vol. **77**, p. 253 (1987)

"Submicron Heterostructures of Diluted Magnetic Semiconductors", R.L. Gunshor, L.A. Kolodziejski, N. Otsuka, S. Datta, and A.V. Nurmikko, Proc. Mat. Res. Soc. vol **89**, p. 123 (1987)

"Frustrated Antiferromagnetism at Heterointerfaces in a Semiconductor Superlattice: MnSe/ZnSe", S.-K. Chang, D. Lee, H. Nakata, A.V. Nurmikko, L.A. Kolodziejski, and R.L. Gunshor, J. Appl. Phys. **62**, 4838 (1986)

"Exciton-Optical Phonon Coupling in Resonant Raman Scattering from CdTe/(Cd,Mn)Te Quantum Wells", S.-K. Chang, H. Nakata, A.V. Nurmikko, R.L. Gunshor, and L.A. Kolodziejski, Appl. Phys. Lett. **51**, 667 (1987)

"Stark Shifts on Exciton Luminescence in Quantum Wells: Effect of Coulomb Interaction", J.W. Wu and A.V. Nurmikko, Phys. Rev. **B36**, 4902 (1987)

"Electric Field Induced Shifts in Exciton Luminescence in ZnSe/(Zn,Mn)Se Superlattices", Qiang Fu, A.V. Nurmikko, L.A. Kolodziejski, R.L. Gunshor, and J.-W. Wu, Appl. Phys. Lett.

51, 578 (1987)

"Resonant Raman Scattering and Exciton-Phonon Interaction in CdTe/(Cd,Mn)Te Quantum Wells", S.-K. Chang, H. Nakata, A.V. Nurmikko, L.A. Kolodziejski, and R.L. Gunshor, *J. de Physique C5*, 345 (1987)

"Magnetic and Electronic Aspects of MnSe/ZnSe Superlattices Near Monolayer Limit, S.-K. Chang, H. Nakata, L. Kolodziejski, and R.L. Gunshor, *J. de Physique C5*, 311 (1987)

"Control of Carrier Lifetime in PbTe doping superlattices", G. Bauer, J. Oswald, W. Goltsos, and A.V. Nurmikko, *J. Appl. Phys.* **63**, 2179 (1988)

"Bandoffsets and Excitons in CdTe/(Cd,Mn)Te Quantum Wells", S.-K. Chang, A.V. Nurmikko, J.-W. Wu, L.A. Kolodziejski, and R.L. Gunshor, *Phys. Rev.* **B37**, 1191 (1988)

"Quasi-Two Dimensional Excitons in Selected II-VI Compound Semiconductor Superlattices, A.V. Nurmikko, *Surface Science* **196**, 632 (1988)

"Exciton Tunneling Lifetime Enhancement by Coulomb Interaction in a Quantum Well with a Perpendicular Field", J.-W. Wu and A.V. Nurmikko, *Phys. Rev.* **B37**, 2711 (1988)

"Exciton Trapping from Atomic Layer Epitaxial ZnTe Within ZnSe/(Zn,Mn)Se Heterostructures", L.A. Kolodziejski, R.L. Gunshor, Q. Fu, D. Lee, A.V. Nurmikko, and N. Otsuka, *Appl. Phys. Lett.*, **52**, 1080 (1988)

"Semimagnetic and Magnetic Semiconductor Superlattices", R.L. Gunshor, L.A. Kolodziejski, A. Nurmikko, and N. Otsuka, *Ann. Rev. of Mat. Science* **18**, 325 (1988)

"II-VI/III-V Heterostructures", L.A. Kolodziejski, R.L. Gunshor, A.V. Nurmikko, and N.

Otsuka. Materials Research Society Proc. vol. 102, 113 (1988)

"Transient Electronic Phenomena in Highly Excited II-VI Compound Semiconductor Quantum Well: CdTe/(Cd,Mn)Te, Proc. SPIE. vol. 942, 241 (1988)

"Control of Carrier Lifetime in PbTe Superlattices by External Photoinjection", J. Oswald, G. Bauer, W. Goltsos, and A.V. Nurmikko, Superlattices and Microstructures 4, 159 (1988)

"The Role of Electron-Hole Coulomb Interaction in Quantum Confined Stark Effect", J-W. Wu and A.V. Nurmikko, Superlattices and Microstructures 4, 81 (1988)

"Exchange Interaction and Strongly Localized Excitons in (Zn,Mn)Se Based Layered Microstructures", A.V. Nurmikko, Q. Fu, D. Lee, R.L. Gunshor, and L.A. Kolodziejski, Proc. 19th Int. Conf. Physics of Semiconductors, Warsaw (1988), p. 1523

"Physics and Engineering in Diluted Magnetic Semiconductor Superlattices", A.V. Nurmikko, R.L. Gunshor, and L.A. Kolodziejski, J. of Crystal Growth, 95, 589 (1989)

"Isoelectronic Delta Doping in a ZnSe Superlattice: Te as an Efficient Hole Trap", Q. Fu, D. Lee, A.V. Nurmikko, R.L. Gunshor, and L.A. Kolodziejski, Phys. Rev B39, 3173 (1989)

"Radiative Recombination in PbTe Quantum Wells", E.T. Heyen, M. Hagerott, A.V. Nurmikko, and D.L. Partin, Appl. Phys. Lett., 54, 653 (1989)

"Molecular-Beam Epitaxy of InSb/CdTe Heterostructures", J. Glenn, Sungki O, L. Kolodziejski, R. Gunshor, M. Kobayashi, D. Li, N. Otsuka, M. Haggerott, N. Pelekanos, and A.V. Nurmikko, J. Vac. Sci. and Techn. B7, 249 (1989)

"Donors and Excitons Bound to a Thin Repulsive Layer", W. Trzeciakowski, P. Hawrylak, G.

Aers, and A. Nurmikko, Solid State Comm. (in press)

The research results have been also presented in a substantial number of domestic and international conferences; examples of invited presentations at major meetings include:

(1987)

- American Physical Society, New York, March
- Society of Photoinstrumentation Engineering, Florida, March
- American Physical Society, New York Section, April
- International Quantum Electronics Conference, Baltimore, April
- U.S.-Japan Seminar on Quantum Electronics, Monterey, July 1987
- Electronic Properties of Two Dimensional Systems, Santa Fe, July 1987
- Optical Society of America Annual Meeting, Rochester, October 1987
- Int. Conf. on Semimagnetic Semiconductors, Jablonna, Poland, Oct 1987

(1988)

- Advances in Semiconductors and Superconductors (SPIE), Newport Beach, CA, March
- International Quantum Electronics Conference (July, Tokyo)

- International Conference on Semiconductor Physics (August, Warsaw, Poland)
- International Conference on Molecular Beam Epitaxy (September, Sapporo, Japan)
- U.S. - Soviet Seminar on Lower Dimensional Systems (June, Moscow)
- NATO Workshop on Optical Switching in Lower Dimensional Systems (October, Marbella, Spain)

(1989)

- Society of Photoinstrumentation Engineering, Los Angeles, CA, , January
- Material Research Society, San Diego, CA, March
- Summer School on Micro and Optoelectronics, Helsinki, Finland, June
- International Conference on Two-Six Compounds, Berlin, FRG, September
- Max-Planck Institute, Stuttgart, September
- Material Research Society, Boston, MA, November

**Statement for Unexpended funds and Patents and Inventions**

- (1) No unexpended or unobligated funds remain of the contract
- (2) No patents and inventions derived from the subject contract